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From THF to Furan: Activity Tuning and Mechanistic Insight via Sidearm Donor Replacement in Group IV Amine Bis(phenolate) Polymerization Catalysts

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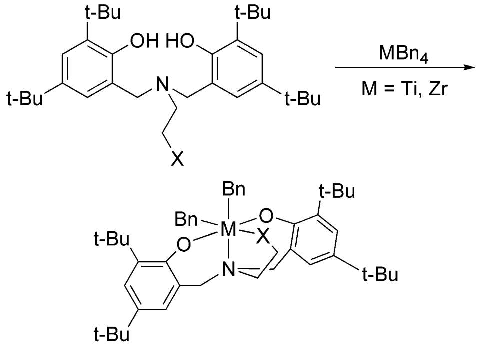
Summary: Weakening the sidearm donor of amine bis(phenolate) titanium and zirconium polymerization catalysts causes a 10-fold enhancement in activity of the former and no difference in activity of the latter, while increasing the termination to propagation ratios in both.

Group IV cyclopentadienyl-free complexes are attracting an ever-increasing amount of attention as catalysts for α-olefin polymerization,[1] since they are highly versatile, may exhibit novel polymerization modes, and lead to previously inaccessible polymers.[2] Yet, in contrast to the extensively studied metallocenes,[3] a thorough structure−activity understanding that may lead to control of catalyst activity and well-defined polymers is lacking. Recently, we introduced a family of olefin polymerization catalysts based on group IV metal complexes of amine bis(phenolate) ligands[4] (Scheme 1). These complexes possess a "rigid" [ONO] core, thereby allowing accurate structure−activity relationship study by varying several peripheral parameters. The most critical parameter was found to be the sidearm donor, as its absence led to fast catalyst deactivation in the zirconium series and to oligomerization in the titanium series.

Scheme 1



Ligands bearing a *strong* sidearm donor led to some remarkable reactivities. Especially when this donor was a THF group, the corresponding zirconium dibenzyl complex exhibited a very high activity in polymerization of 1-hexene, and the corresponding titanium dibenzyl complex led to a slow but living polymerization of 1-hexene at room temperature for an exceptionally long time of 6 days.[4f] Herein we introduce an amine bis(phenolate) ligand featuring a *weak* sidearm donor, i.e., furan, and study the activity of its resulting catalysts in polymerization of 1-hexene. The different electronic properties combined with similar steric bulks of THF and furan shed light on the intricate parameters controlling the activity of these catalysts (Figure 1).

The ligand precursor was prepared by condensing 2,4-di-*tert*-butylphenol, formaldehyde, and 2-(aminomethyl)-furan and reacted cleanly with the corresponding tetrabenzylmetal precursors to yield the dibenzyl zirconium and titanium complexes **1a**,**b**, respectively, in high yields. The ^{1}H NMR and ^{13}C NMR spectra indicated that both complexes are C_s symmetrical. Pale yellow crystals of **1a** suitable for an X-ray structure determination were obtained upon recrystallization from toluene.[5] The crystal structure was consistent with the NMR data and confirmed the binding of the furan oxygen to the zirconium (Figure 2). The structure reveals a slightly distorted octahedral geometry, with the phenolate oxygens being mutually trans (157.86°) and the benzyl groups mutually cis (108.30°). As expected for

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(2) For an example of living and highly active ethylene polymerization see: (a) Mitani, M.; Mohri, J.; Yoshida, Y.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327. For an example of living and syndiotactic polymerization of propylene see: (b) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134. For examples of living polymerization of high α-olefins see: (c) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (d) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (e) Jeon, Y. M.; Park, S. J.; Heo, J.; Kim, K. *Organometallics* **1998**, *17*, 7**,** 3161. (f) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746. For an example of living and isotactic polymerization of 1-hexene see: (g) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.

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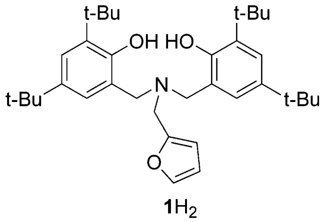
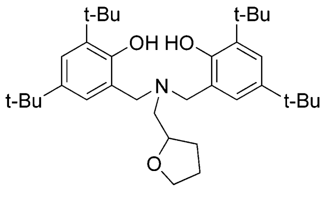


1H_2



2H_2

Figure 1. The two ligand precursors described in this work. **1a** and **2a** denote the corresponding zirconium dibenzyl complexes; **1b** and **2b** denote the corresponding titanium dibenzyl complexes.

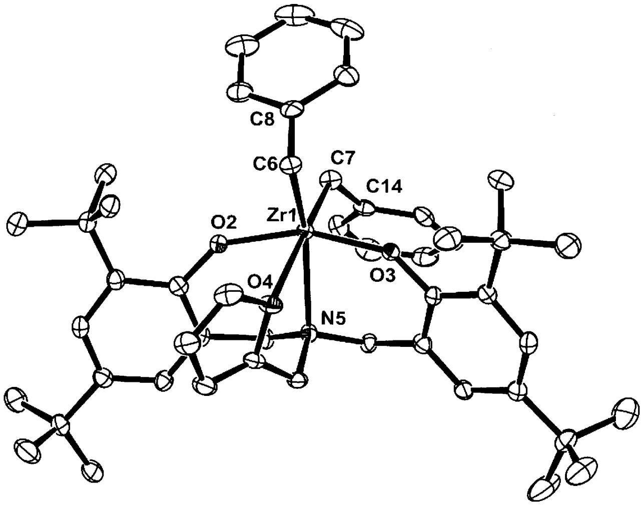


Figure 2. ORTEP view of **1a** (50% probability ellipsoids). Key atoms are labeled. Selected bond distances (Å) and angles (deg): Zr(1)−O(2) = 2.000(2), Zr(1)−O(3) = 1.978(2), Zr(1)−O(4) = 2.684(2), Zr(1)−N(5) = 2.434(2), Zr(1)−C(6) = 2.273(3), Zr(1)−C(7) = 2.299(3); O(3)−Zr(1)−O(4) = 85.60(6), O(2)−Zr(1)−O(4) = 80.11(6), C(8)−C(6)−Zr(1) = 98.6(2), C(14)−C(7)−Zr(1) = 119.5(2).

the weak furan donor, the Zr−O bond distance was found to be exceptionally long (2.68 Å). This bond is longer than all other M−O bonds, and most M−N bonds reported thus far, for metal−sidearm donor bonds in group IV metal complexes of this ligand family.[4] In contrast, the Zr−O bond distance for the complex bearing a THF sidearm donor (**2a**) was found to be very short (2.37 Å).[4f] Significantly, except for the sidearm donor-to-metal bond distances, the bindings of these two [ONOO]-type ligands to the zirconium are essentially identical. A narrower Zr−C−C angle for the top benzyl group in **1a** relative to **2a** may indicate a partial η^2 binding resulting from a more electron-deficient metal center. On the basis of the low steric demands of the furan group, and on previous crystal structures, we propose that the furan oxygen is bound to the titanium center in **1b** and that its binding is weak.

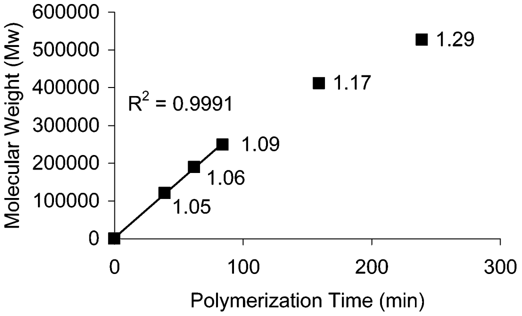


Figure 3. "Semi-living" polymerization of neat 1-hexene by **1b**/$B(C_6F_5)_3$.

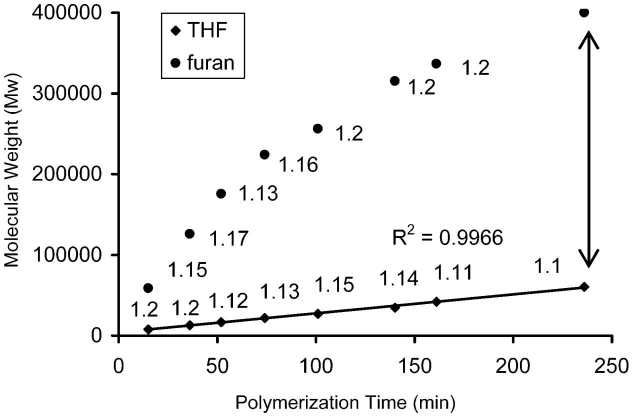


Figure 4. M_w dependence on time (min) in a mixed-catalyst (**1b** and **2b**) 1-hexene polymerization experiment. Each vertical pair of points represents a single aliquot taken at a given time.

The polymerization studies were performed in neat 1-hexene by activating the precatalysts **1a** and **1b** by addition of approximately equimolar amounts of $B(C_6F_5)_3$. The catalytic system **1a**/$B(C_6F_5)_3$ was found to be almost as active in 1-hexene polymerization as **2a**/$B(C_6F_5)_3$:[4f] that is, weakening the donor on the sidearm *electronically* does not appear to affect the polymerization rate significantly for zirconium. However, the molecular weight of the poly(1-hexene) obtained was reduced substantially: M_w = 15 000−25 000 for **1a**/$B(C_6F_5)_3$, relative to M_w = 80 000−120 000 produced by **2a**/$B(C_6F_5)_3$. This difference may stem from an increased termination−reactivation pathway in **1a/**$B(C_6F_5)_3$ as a result of the less tightly bound sidearm donor.

Surprisingly, the sidearm donor replacement had a much more pronounced effect for the titanium complexes. Following addition of $B(C_6F_5)_3$, the titanium precatalyst **1b** was found to be at least 10-fold more active than the corresponding titanium complex bearing THF as a sidearm donor (**2b**),[4f] with the activity corresponding to ca. 200 g $mmol_{cat}^{-1}$ h^{-1}. In fact, this is the most active amine bis(phenolate) titanium catalyst reported so far. In contrast to its zirconium analogue, **1b/**$B(C_6F_5)_3$ produced very high molecular weight poly(1-hexene) (a polymer having M_w = 550 000 was obtained after polymerization of neat 1-hexene at room temperature for 4 h). Although this polymerization

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(5) Crystal data for **1a**·$2C_7H_8$, $C_{63}H_{79}NO_3Zr$, M_r = 989.49, monoclinic, space group $P2_1/n$; a = 16.2970(2) Å; b = 15.7960(2) Å; c = 22.0160(3) Å; β = 101.3020(8)°; V = 5557.62(12) Å^3; Z = 4, D = 1.183 g/cm^3; ρ = 0.242 mm^{-1}; 9396 independent reflections collected; 7537 unique reflections with $I > 2\sigma(I)$; R1($I > 2\sigma(I)$) = 0.0448; wR2($I > 2\sigma(I)$) = 0.1161; R1(all data) = 0.0620; wR2(all data) = 0.1273. Data were collected on a Kappa CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å) at 110 K. For full details concerning crystallographic analysis see the Supporting Information.

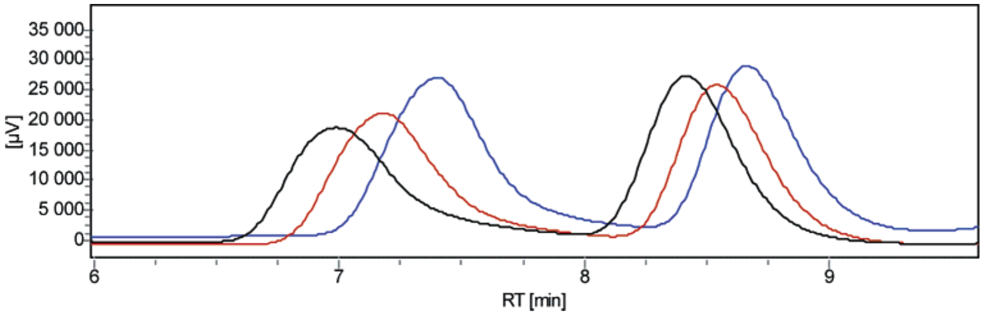

Figure 5. GPC traces of three consecutive aliquots of the mixed-catalyst polymerization experiment (see Figure 3 and Supporting Information), featuring the well-resolved peaks of the low-molecular-weight and high-molecular-weight polymers. Blue line (polymerization time 36 min): M_w(RT = 8.76 min) = 12 900, PDI = 1.20; M_w(RT = 7.41 min) = 126 000, PDI = 1.17. Red line (polymerization time 52 min): M_w(RT = 8.55 min) = 16 900, PDI = 1.12; M_w(RT = 7.19 min) = 175 700, PDI = 1.13. Black line (polymerization time 74 min): M_w(RT = 8.42 min) = 21 800, PDI = 1.12; M_w(RT = 7.00 min) = 223 900, PDI = 1.16.

cannot be defined as truly living (a slow broadening of PDI was observed, and the final polymer sample had a PDI of 1.37), very narrow polydispersities (1.05−1.09) were recorded for the first 2 h of polymerization, after which the molecular weight of the polymer was higher than 200 000 (Figure 3). Evidently, reducing the strength of the sidearm donor in the titanium series resulted in a significant increase in propagation rate but concurrently encouraged termination to some extent, thereby bringing about a reduction of the living polymerization character.

The availability of two structurally related catalysts, both of which undergo almost no termination and feature a 10-fold difference in activity (i.e. **1b** and **2b**), enables the evaluation of possible polymeryl transfer between two propagating species, by GPC monitoring of the progress of a “mixed-catalyst” polymerization experiment. Recently, polymeryl transfer has been investigated by several groups, since, if feasible, it could be employed in the formation of block copolymers.[6−8] The polymerization was performed in neat 1-hexene, using a ca. 7:1 ratio of **2b** to **1b**, respectively, and $B(C_6F_5)_3$ as an activator. During the whole experiment, *two* resolved peaks could be detected in the GPC trace: the low-molecular-weight peak was attributed to the action of **2b**/$B(C_6F_5)_3$ and the high-molecular-weight peak to the action of **1b**/$B(C_6F_5)_3$. Significantly, both catalysts were found to react at their “native” polymerization rates, as evident from the molecular weights. Furthermore, the two catalysts retain their original living character in the presence of each other. Especially, **2b**/$B(C_6F_5)_3$ remained living throughout the experiment, as supported by the linear increase of molecular weight vs time and very narrow polydispersities. **1b**/$B(C_6F_5)_3$ showed living behavior in the first 2−3 h only, after which the polymerization in this system decayed (Figures 4 and 5). All this supports the existence of two independent propagating species that do not communicate with each other under these conditions. We thus propose that an alkyl-bridged dinuclear species is not a viable intermediate in the polymerization pathway of the catalysts of this family.

In conclusion, weakening the sidearm donor of amine bis(phenolate) ligands affected the activity of the resulting polymerization catalysts. An apparent increase in termination rate for both zirconium and titanium complexes led to a decrease in molecular weights of the resulting poly(1-hexene) (Zr) or to loss of living polymerization character (Ti) and may be associated with the ease of detaching the sidearm donor from the metal. The similarity in polymerization rates for zirconium in contrast to the unexpected 10-fold increase in polymerization rate for titanium may reflect the latter’s higher response to steric effects, as the smaller and remote furan in comparison to THF leads to a more open site. A polymeryl exchange between two propagating titanium species does not seem to occur; thus, the possibility of alkyl-bridged dinuclear species in this system is unlikely. We are investigating further structure−activity relationships in this family.

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Supporting Information Available: Text and tables giving synthetic details and spectroscopic data for **1a**,**b**, polymerization procedures, and crystallographic data for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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